Universal Correction of Density Functional Theory to include London Dispersion (up to Lr, element 103)

Hyungjun Kim[a,†,*], *Jeong-Mo Choi*[b,†,‡], *and William A. Goddard, III*[a,c,d,*]

[a] Graduate School of Energy Environment Water Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701, Republic of Korea

[b] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701, Republic of Korea

[c] Materials and Process Simulation Center, Beckman Institute, California Institute of Technology, Pasadena, CA 91125

[d] World Class University Professor, EEWS/KAIST, Daejeon, 305-701, Republic of Korea

[†]These authors contribute equally

[‡]Currently at: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street Cambridge, MA 02138

[*]To whom correspondence should be addressed:

E-mail: linus16@kaist.ac.kr and wag@wag.caltech.edu

Computational details

The universal low-gradient (*ulg*) method is implemented into the VASP 5.2.11.[1,2] For the calculations of crystal systems, we used projector augmented wave (PAW) pseudopotentials developed by Kresse *et al*[3] with the exchange-correlation function of Perdew, Burke, and Ernzerhof (PBE).[4] For a plane-wave kinetic energy cutoff, 700 eV is used for hydrocarbon systems and 1000 eV for other systems. We set a van der Waal's (vdW) radius of 35 Å and consider all pairwise vdW interactions whose distances are less than this vdW radius. For the sampling in the reciprocal space, we used a $3 \times 3 \times 3$ Monkhorst-Pack grid for most calculations, but a $6 \times 6 \times 2$ grid is used for a graphite and h-BN, and a $5 \times 3 \times 1$ grid for a C_8K. For the zero-point energy computation, we expand our unit cells as twice in each cell length (totally eight times in volume) and compute the vibrational frequencies, since the VASP only provides zone-centered (Γ-point) frequency calculations.

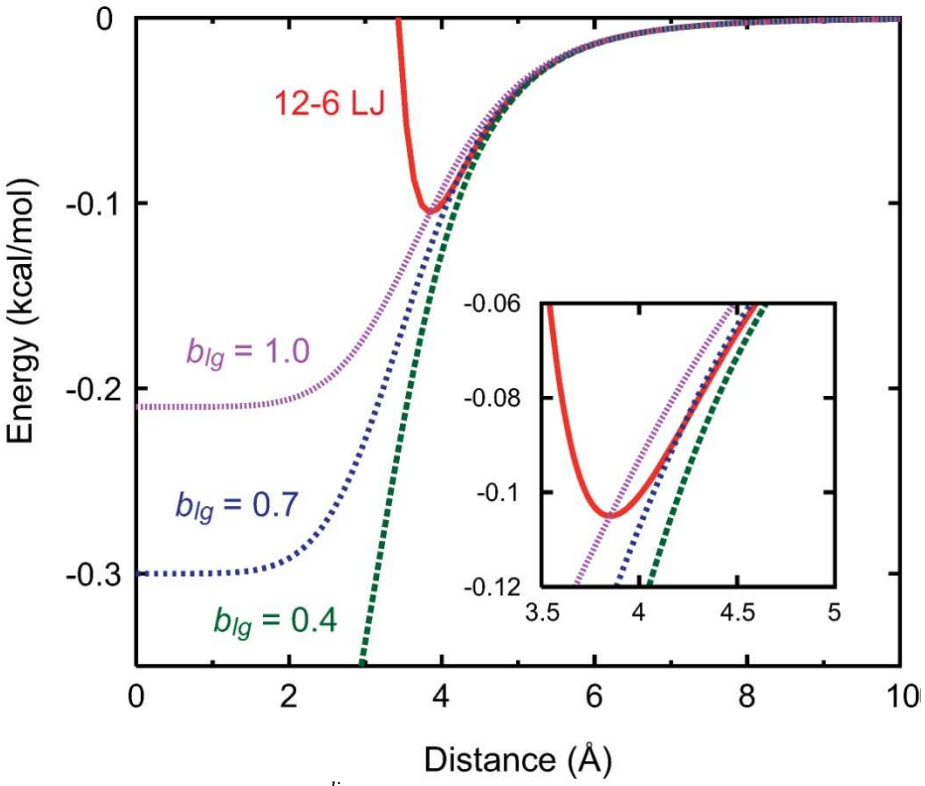

Fig. S1 Plots of the dispersion energy (E^{disp}) of DFT-*ulg* method as a function of b_{lg} = 0.4 (green line), 0.7 (blue line), and 1.0 (magenta line) compared with a 12-6 Lennard-Jones potential (red line).

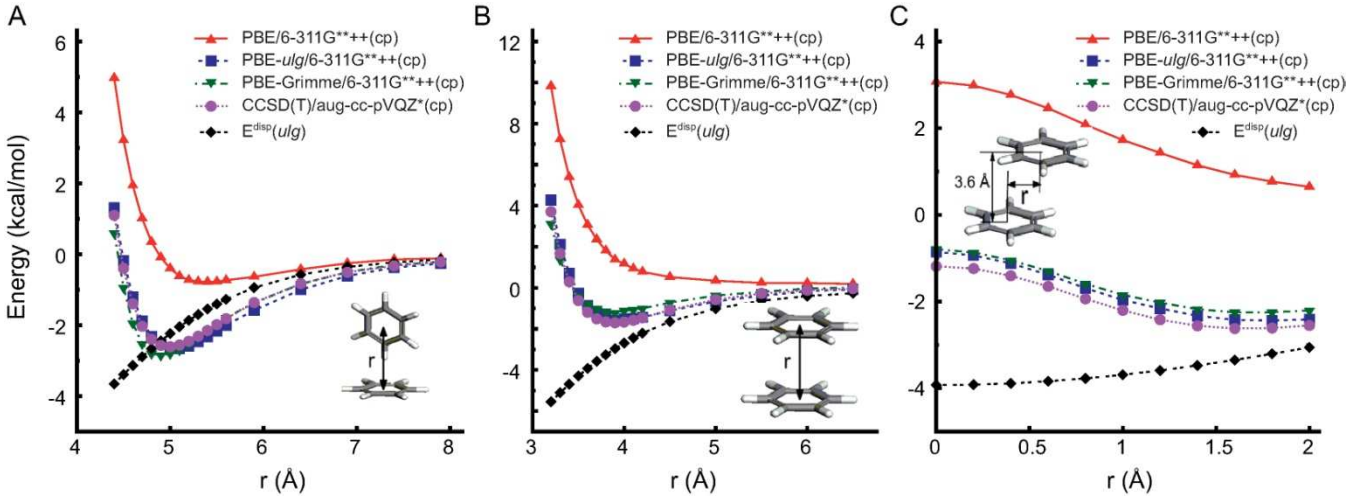

Fig. S2 Binding energy curves of benzene dimers in the a) T-shaped configuration, b) sandwich configuration, and c) parallel-displaced configuration as a function of distance calculated using the PBE-*ulg* method (blue) compared with PBE (red), PBE with Grimme's correction (green), and high level wavefunction calculation, CCSD(T) (magenta).[5]

Table S1. Lennard Jones parameters (R_0 and D_0) of universal force field (UFF) from H (Z=1) to Lr (Z=103).[6] Dispersion coefficients ($C6$) are given as $2D_0R_0^6$. (Units: R_0 in Å, D_0 in kcal/mol, and C6 in kcal Å^6/mol)

Atom	R_0	D_0	$C6$	Atom	R_0	D_0	$C6$	Atom	R_0	D_0	$C6$
H	2.886	0.044	50.85	Kr	4.141	0.220	2218.63	Lu	3.640	0.041	190.73
He	2.362	0.056	19.45	Rb	4.114	0.040	387.86	Hf	3.141	0.072	138.28
Li	2.451	0.025	10.84	Sr	3.641	0.235	1095.02	Ta	3.170	0.081	164.39
Be	2.745	0.085	72.73	Y	3.345	0.072	201.72	W	3.069	0.067	111.97
B	4.083	0.180	1667.93	Zr	3.124	0.069	128.28	Re	2.954	0.066	87.71
C	3.851	0.105	684.95	Nb	3.165	0.059	118.61	Os	3.120	0.037	68.26
N	3.660	0.069	331.72	Mo	3.052	0.056	90.52	Ir	2.840	0.073	76.61
O	3.500	0.060	220.59	Tc	2.998	0.048	69.70	Pt	2.754	0.080	69.81
F	3.364	0.050	144.92	Ru	2.963	0.056	75.79	Au	3.293	0.039	99.46
Ne	3.243	0.042	97.71	Rh	2.929	0.053	66.93	Hg	2.705	0.385	301.64
Na	2.983	0.030	42.27	Pd	2.899	0.048	56.98	Tl	4.347	0.680	9176.49
Mg	3.021	0.111	168.76	Ag	3.148	0.036	70.07	Pb	4.297	0.663	8347.10
Al	4.499	0.505	8375.63	Cd	2.848	0.228	243.34	Bi	4.370	0.518	7215.20
Si	4.295	0.402	5047.02	In	4.463	0.599	9467.13	Po	4.709	0.325	7087.38
P	4.147	0.305	3102.66	Sn	4.392	0.567	8139.30	At	4.750	0.284	6523.94
S	4.035	0.274	2365.06	Sb	4.420	0.449	6695.92	Rn	4.765	0.248	5805.76
Cl	3.947	0.227	1716.56	Te	4.470	0.398	6349.77	Fr	4.900	0.050	1384.13
Ar	3.868	0.185	1239.14	I	4.500	0.339	5629.95	Ra	3.677	0.404	1996.98
K	3.812	0.035	214.79	Xe	4.404	0.332	4844.53	Ac	3.478	0.033	116.82
Ca	3.399	0.238	734.03	Cs	4.517	0.045	764.44	Th	3.396	0.026	79.76
Sc	3.295	0.019	48.63	Ba	3.703	0.364	1876.95	Pa	3.424	0.022	70.90
Ti	3.175	0.017	34.83	La	3.522	0.017	64.90	U	3.395	0.022	67.37
V	3.144	0.016	30.91	Ce	3.556	0.013	52.57	Np	3.424	0.019	61.23
Cr	3.023	0.015	22.90	Pr	3.606	0.010	43.97	Pu	3.424	0.016	51.56
Mn	2.961	0.013	17.52	Nd	3.575	0.010	41.75	Am	3.381	0.014	41.82
Fe	2.912	0.013	15.85	Pm	3.547	0.009	35.85	Cm	3.326	0.013	35.20
Co	2.872	0.014	15.71	Sm	3.520	0.008	30.44	Bk	3.339	0.013	36.03
Ni	2.834	0.015	15.54	Eu	3.493	0.008	29.06	Cf	3.313	0.013	34.38
Cu	3.495	0.005	18.23	Gd	3.368	0.009	26.27	Es	3.299	0.012	30.94
Zn	2.763	0.124	110.34	Tb	3.451	0.007	23.65	Fm	3.286	0.012	30.21
Ga	4.383	0.415	5884.46	Dy	3.428	0.007	22.72	Md	3.274	0.011	27.10
Ge	4.280	0.379	4659.42	Ho	3.409	0.007	21.97	No	3.248	0.011	25.83
As	4.230	0.309	3540.22	Er	3.391	0.007	21.29	Lr	3.236	0.011	25.26
Se	4.205	0.291	3217.50	Tm	3.374	0.006	17.70				
Br	4.189	0.251	2712.48	Yb	3.355	0.228	650.31				

Table S2. Comparison of binding energies of Hobza's non-covalent 22 complexes.[7] The binding energy was calculated with PBE-ulg and PBE methods with 6-31(+,+)G(d,p) basis set (with counter-poise correction) based on the structures in the reference 7.

	PBE	PBE-*ulg*	Reference
Ammonia dimer	3.51	4.04	3.17
Water dimer	5.57	5.99	5.02
Formic acid dimer	17.49	18.86	18.61
Formamide dimer	14.52	15.94	15.96
Uracil dimer (hydrogen bond)	18.41	20.40	20.47
2-pyridoxine 2-aminopyridine	15.37	17.76	16.71
Adenine-thymine (Watson-Crick pair)	14.33	16.88	16.37
Methane dimer	0.05	0.66	0.53
Ethene dimer	0.40	1.64	1.51
Benzene-methane	0.00	1.45	1.5
Benzene dimer (parallel-displaced)	-2.23	1.84	2.73
Pyrazine dimer	-0.79	2.90	4.42
Uracil dimer (stack)	2.76	7.91	9.88
Indole-benzene (stack)	-2.35	3.40	5.22
Adenine-thymine (stack)	1.19	8.64	12.23
Ethene-ethyne	1.26	1.88	1.53
Benzene-water	2.11	3.42	3.28
Benzene-ammonia	1.04	2.38	2.35
Benzene-HCN	2.85	4.45	4.46
Benezene dimer (T-shape)	-0.06	2.37	2.74
Indole-benzene (T-shape)	2.08	5.34	5.73
Phenol dimer	4.13	6.79	7.05
Mean absolute error (MAE)	2.80	0.70	-

Table S3. Equilibrium cell volume of simple molecular crystal systems, N_2, O_2, CO and CO_2, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments. For CO_2 crystal, we estimated the contribution of lattice vibrations (VIB) using MD simulations using DREIDING force-fields. [a]VIB = 1.01 %.

	N_2	O_2	CO	CO_2
PBE	180.04	69.38	178.96	218.17
PBE-*ulg*	179.89	69.35	178.99	179.93
Experiments	179.79 (4.2 K)[8]	69.11 (7 K)[9]	179.98 (8 K)[10]	177.88 (150 K)[11] 176.10 (0 K)[a]

Table S4. Heat of sublimation ΔH_{sub} of simple molecular crystal systems, N_2, O_2, CO and CO_2, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments. ZPEs are considered by calculating phonon vibrations consistently.

	N_2	O_2	CO	CO_2
PBE	0.09	0.04	0.18	2.15
PBE-*ulg*	1.13	1.41	1.46	4.61
Experiments	1.66[9]	2.07[9]	1.99[10]	6.27[12]

Table S5. Equilibrium cell volume of halogen molecular crystal systems, F_2, Cl_2, Br_2 and I_2, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments.

	F_2	Cl_2	Br_2	I_2
PBE	126.47	282.48	317.30	409.03
PBE-*ulg*	126.32	236.23	270.06	345.13
Experiments	128.38 (23 K)[13]	220.24 (22 K)[14]	255.08 (5 K)[14]	324.97 (5 K)[15]

Table S6. Heat of sublimation ΔH_{sub} of halogen molecular crystal systems, F_2, Cl_2, Br_2 and I_2, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments. ZPEs are considered by calculating phonon vibrations consistently. For I_2 crystal, we estimated the contribution of lattice vibrations (VIB) using MD simulations using DREIDING force-fields. [a]VIB = 15.39 %.

	F_2	Cl_2	Br_2	I_2
PBE	0.25	2.02	5.87	8.52
PBE-*ulg*	1.36	5.73	10.34	14.42
Experiments	2.19 (0 K)[16]	7.17 (0 K)[16]	11.07 (0 K)[16]	14.92 (RT)[17] 17.63 (0 K)[a]

Table S7. Lattice constant *a* of rare gas face-centered-cubic crystal systems, Ne, Ar, Kr and Xe, calculated using PBE-*ulg* method, compared with conventional PBE calculations, PBE calculations with Grimme's correction, adiabatic connection fluctuation-dissipation theory (ACFDT) calculations, *ab initio* CCSD(T) calculations, and experiments. [a]All values are obtained by extrapolation to 0 K.

	Ne	Ar	Kr	Xe
PBE	4.643	5.936	6.403	7.052
PBE-*ulg*	4.464	5.618	6.056	6.576
PBE-Grimme[18]	4.23	5.38	5.64	6.06
ACFDT[19]	4.5	5.3	5.7	-
CCSD(T)[20]	4.468	5.311	5.633	6.111
Experiments[a]	4.464[21]	5.300[22]	5.646[23]	6.132[24]

Table S8. Heat of sublimation ΔH_{sub} of rare gas face-centered-cubic crystal systems, Ne, Ar, Kr and Xe, calculated using PBE-*ulg* method, compared with conventional PBE calculations, PBE calculations with Grimme's correction, adiabatic connection fluctuation-dissipation theory (ACFDT) calculations, *ab initio* CCSD(T) calculations, and experiments. ZPEs are considered by calculating phonon vibrations consistently.

	Ne	Ar	Kr	Xe
PBE	0.40	0.45	0.48	0.63
PBE-*ulg*	0.69	1.38	1.62	2.09
PBE-Grimme[18]	1.34	2.03	3.34	5.03
ACFDT[19]	0.39	1.91	2.58	-
CCSD(T)[20]	0.47	1.85	2.68	3.80
Experiments	0.46[23]	1.85[25]	2.68[25]	3.79[25]

Table S9. Equilibrium cell volume of poly aromatic hydrocarbon crystal systems, naphathalene, anthracene, and phenanthracene, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments. [a]All values are obtained by extrapolation to 0 K. For phenanathracene crystal, we estimated the contribution of lattice vibrations (VIB) using MD simulations using DREIDING force-fields. [a]VIB = 6.17 %.

	Naphthalene	Anthracene	Phenanthracene
PBE	380.23	515.49	524.51
PBE-*ulg*	344.41	451.55	461.68
Experiments	342.3 (12 K)[26]	455.2 (14 K)[27]	489.7 (RT)[28] 459.5 (0 K)[a]

Table S10. Heat of sublimation ΔH_{sub} of poly aromatic hydrocarbon crystal systems, naphathalene, anthracene, and phenanthracene, calculated using PBE-*ulg* method, compared with conventional PBE calculations and experiments. [a]All values are obtained by extrapolation to 0 K. Zero-point energy (ZPE) and lattice vibration (VIB) are corrected. [b]ZPE = 0.55 kcal/mol,[29] VIB = 16.91 %. [c]ZPE = 2.69 kcal/mol (this work), VIB = 9.19 %. [d]ZPE = 2.34 kcal/mol (this work), VIB = 5.84 %.

	Naphthalene	Anthracene	Phenanthracene
PBE	0.89	1.75	1.52
PBE-*ulg*	18.93	25.80	24.39
Experiments	15.3-19.6 (RT + ZPE)[17]	20.1-25.0 (RT + ZPE)[17]	20.1-22.9 (RT + ZPE)[17]

18.4-23.5 (0 K)[b]	24.6-30.0 (0 K)[c]	23.6-26.5 (0 K)[d]

Table S11. Dependence of elastic constant, C_{33} on the damping constant in Grimme's correction, determining the local curvature of E^{disp}. Units of C_{33} values are in GPa. We note that the suggested value by Grimme is 20 Å.[30]

d (Å)	Graphite	*h*-BN	C_8K
10	44.4	54.2	64.7
15	42.4	60.4	66.2
20	42.0	69.0	74.8

REFERENCES

(1) Kresse, G.; Furthmuller, J. *Comput. Mater. Sci.* **1996**, *6*, 15.
(2) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169.
(3) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
(4) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865.
(5) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200.
(6) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.
(7) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985.
(8) Bolz, L. H.; Boyd, M. E.; Mauer, F. A.; Peiser, H. S. *Acta Cryst.* **1959**, *12*, 247.
(9) Freiman, Y. A.; Jodl, H. J. *Phys. Rep.-Rev. Sec. Phys. Lett.* **2004**, *401*, 1.
(10) Janssen, W.; Michiels, J.; Vanderavoird, A. *J. Chem. Phys.* **1991**, *94*, 8402.
(11) Simon, A.; Peters, K. *Acta Crystallogr. Sect. B-Struct. Sci.* **1980**, *36*, 2750.
(12) Steinebrunner, G.; Dyson, A. J.; Kirchner, B.; Huber, H. *J. Chem. Phys.* **1998**, *109*, 3153.
(13) Pauling, L.; Keaveny, I.; Robinson, A. B. *Journal of Solid State Chemistry* **1970**, *2*, 225.
(14) Powell, B. M.; Heal, K. M.; Torrie, B. H. *Mol. Phys.* **1984**, *53*, 929.
(15) Petrillo, C.; Moze, O.; Ibberson, R. M. *Physica B* **1992**, *180*, 639.
(16) Jelinek, G. E.; Slutsky, L. J.; Karo, A. M. *J. Phys. Chem. Solids* **1972**, *33*, 1279.
(17) Chickos, J. S.; Acree, W. E. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537.
(18) Bucko, T.; Hafner, J.; Lebegue, S.; Angyan, J. G. *J. Phys. Chem. A* **2010**, *114*, 11814.
(19) Harl, J.; Kresse, G. *Phys. Rev. B* **2008**, *77*, 8.
(20) Rosciszewski, K.; Paulus, B.; Fulde, P.; Stoll, H. *Phys. Rev. B* **2000**, *62*, 5482.
(21) Batchelder, D. N.; Losee, D. L.; Simmons, R. O. *Phys. Rev.* **1967**, *162*, 767.
(22) Peterson, O. G. B., D. N.; Simmons, R. O. *Phys. Rev.* **1966**, *150*, 703.
(23) McConville, G. T. *J. Chem. Phys.* **1974**, *60*, 4093.
(24) Sears, D. R.; Klug, H. P. *J. Chem. Phys.* **1962**, *37*, 3002.
(25) Schwalbe, L. A.; Crawford, R. K.; Chen, H. H.; Aziz, R. A. *J. Chem. Phys.* **1977**, *66*, 4493.
(26) Natkaniec, I.; Belushkin, A. V.; Dyck, W.; Fuess, H.; Zeyen, C. M. E. *Z. Kristall.* **1983**, *163*, 285.
(27) Chaplot, S. L.; Lehner, N.; Pawley, G. S. *Acta Crystallogr. Sect. B-Struct. Sci.* **1982**, *38*, 483.
(28) Kay, M. I.; Okaya, Y.; Cox, D. E. *Acta Crystallographica Section B-Structural Crystallography and Crystal Chemistry* **1971**, *B 27*, 26.
(29) Day, G. M.; Price, S. L.; Leslie, M. *J. Phys. Chem. B* **2003**, *107*, 10919.
(30) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.